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13. ABSTRACT (Maximum 200 words) In some recent work, we found that carbon-carbon composites made with porous, high-surface-area fibers and liquid matrix precursors were more resistant to oxidation than comparable composites made with non-porous, low-surface-area fibers. The experiments described here were designed in an attempt to assess the relative importance of surface chemistry and porosity of the fibers for the resulting oxidation behavior of the composites. All composites except the high-temperature-related pitch-matrix-precursor composites showed a consistent effect of the surface treatments. Generally, the composites made with fibers given the (an) treatment had superior oxidation resistance. When this is taken in conjunction with the apparent lack of a strong influence from crystallinity, it suggests that chemical adhesion is the dominant mechanism by which the oxidation resistance is improved. Clearly, the larger the surface area for adhesion to occur, the more pronounced is the effect.					
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A NEW APPROACH TOWARD THE UNDERSTANDING OF OXIDATION  
OF CARBON/CARBON COMPOSITES

Final Technical Report  
(Grant No. F49620-92-J-0306)

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Air Force Office of Scientific Research  
Building 410  
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March 8, 1996

# A NEW APPROACH TOWARD THE UNDERSTANDING OF OXIDATION OF CARBON/CARBON COMPOSITES

Final Technical Report  
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In the proposal on which this research was based, we asked the following three questions:

- Is there a synergism between the fibers and the matrix during oxidation of C/C composites?
- Do the fibers or does the matrix have more reactive sites?
- Is the reactivity of a carbon site dependent on the nature of the carbon fiber (or matrix) precursor?

In the research performed by the two students supported on this grant, much progress has been made in providing answers to the first question. A partial answer to the second question can also be given. The third question proved to be too much of a challenge for both students (within the time frame available).

Stephen C. Kokenes has completed his research and defended his M. S. thesis in Materials. The topic of his thesis was the oxidation behavior of carbon/carbon composites prepared by liquid-phase impregnation/carbonization (LPIC). A copy of the paper that he presented at the 22nd Biennial Conference on Carbon (San Diego, CA (July 1995) is attached. A manuscript is being prepared for submission to a peer-reviewed journal. The most valuable contribution from this research is the improved understanding of the effects of both physical properties (porosity) and chemical properties (surface functionalities) of the fibers on the oxidation resistance of the composite.

Farhat A. Quli has also completed his research and defended his M. S. thesis in Materials. The topic of his thesis was the oxidation behavior of C/C composites prepared by chemical vapor deposition/infiltration (CVD/CVI). A copy of the paper that he presented at the 22nd Biennial Conference on Carbon (San Diego, CA (July 1995) is attached. A manuscript is being prepared for submission to a peer-reviewed journal. The most valuable contribution from this research is the confirmation of the general validity of the concept of oxidation resistance enhancement by tailoring the porous structure of the fibers and inducing enhanced matrix graphitization.

# FURTHER STUDIES OF THE OXIDATION RESISTANCE OF CARBON-CARBON COMPOSITES PREPARED BY LIQUID PHASE IMPREGNATION/CARBONIZATION

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## INTRODUCTION

In some recent work, we found that carbon-carbon composites made with porous, high-surface-area fibers and liquid matrix precursors were more resistant to oxidation than comparable composites made with non-porous, low-surface-area fibers [1]. The porous fibers were produced by an oxidative activation process. This created porosity and also modified the surface chemistry of the fibers. Either consequence of the activation process could be responsible for the observed improvements in oxidation resistance.

If the porosity is the controlling factor, then the oxidation resistance could arise from the following mechanisms. The liquid matrix precursor would flow into the pores, mechanically locking together the fiber and matrix [2]. This alone could serve by preventing large cracks from opening at the fiber-matrix interface. It is also possible that the increased constraint of the matrix precursor in the pores and at the interface would promote stress-graphitization of the matrix carbon [3]. This would reduce reactivity by the fact that more crystalline carbon is less reactive.

The surface chemistry could also be responsible for the improvements. If this is so, then adhesion of the matrix to the fibers could produce effects similar to those postulated in the porosity-controlled case. Fiber-matrix adhesion is a well known effect in polymer-matrix composites [4]. It is known that although the chemical bonding between the fibers and a polymeric matrix may not be conserved upon pyrolysis, the existence of that bonding will affect the final composite's microstructure [5].

The experiments described here were designed in an attempt to assess the relative importance of surface chemistry and porosity of the fibers for the resulting oxidation behavior of the composites.

## EXPERIMENTAL

Carbon-carbon composites were produced using VCL fibers (Amoco) and two matrix precursors: A240 petroleum pitch (Ashland), and SC1008 phenol-

formaldehyde resin (Borden). The pitch-based composites were prepared by a pressure impregnation process at 2000 psi and 500 °C followed by a 1000 °C heat treatment at ambient pressure. The resin-based composites were cured and subsequently given the same 1000 °C heat treatment. Some composites were then heat-treated to 2850 °C.

Initially, the VCL fibers had been given certain treatments. These treatments were as follows: 1000 °C in inert atmosphere, activation in CO<sub>2</sub> at 850 °C to a level of 25% burnoff, and nitration for 30 minutes in hot concentrated HNO<sub>3</sub>. The four categories of fiber were then: heat treated only (ut), activated then heat treated (at), activated then nitrated (an), and nitrated only (un).

The oxidation resistance of the composites was tested in flowing air in a Cahn 2000 TGA apparatus. The composites' crystal structure was investigated by X-ray diffraction (Rigaku Geigerflex). The composites were also examined with a scanning electron microscope.

## RESULTS

The effect of the fiber surface treatments on the oxidation resistance of the composites is most visible in the 1000 °C samples (Figure 1). In composites from both matrix precursors, the (an) treatment appeared to have the largest effect on oxidation resistance. This was followed by the (un) treatment. In both cases, the composites made with (ut) fibers had the poorest oxidation resistance. This order of reactivity is repeated in the 2850 °C resin-matrix-precursor composites (Figure 2). The reactivities of the 2850 °C pitch-matrix-precursor composites are very similar regardless of fiber treatment.

The XRD experiments did not show any strong correlation between crystallinity and oxidation resistance (Table 1). The SEM experiments, however, appeared to show that the more oxidation-resistant composites had better fiber-matrix coupling and a thicker matrix layer around the fibers.

## DISCUSSION

All composites except the high-temperature-treated pitch-matrix-precursor composites showed a consistent effect of the surface treatments. Generally, the composites made with fibers given the (an) treatment had superior oxidation resistance. When this is taken in conjunction with the apparent lack of a strong influence from crystallinity, it suggests that chemical adhesion is the dominant mechanism by which the oxidation resistance is improved. Clearly, the larger the surface area for adhesion to occur, the more pronounced is the effect.

## ACKNOWLEDGMENT

This study is made possible by a grant from the U.S. Air Force Office of Scientific Research (F49620-92-J-0306; Dr. A. Pechenik, program manager).

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Table 1. XRD data for the composites studied.

Sample	$d_{002}$ , Å	$L_c$ , Å	$L_a$ , Å
SP-1 graphite	3.34	158	399
vanpht	3.37	161	253
vunpht	3.38	158	252
vatpht	3.37	161	324
vutpht	3.38	155	219
vanrht	3.39	80	116
vunrht	3.37	143	72
vatrht	3.36	134	91
vutrht	3.38	149	83
vanpit	3.53	11	49
vunpit	3.49	11	51
vatpit	3.49	14	51
vutpit	3.54	13	60
vunrit	3.95	-	38
vatrit	3.86	-	43
vutrit	4.04	-	43

Note: v = VCL fiber;  
 a/u = activated/unactivated;  
 n/t = nitrated/heat-treated;  
 p/r = pitch/resin (matrix);  
 lt/ht = 1000 °C/2850 °C (heat treatment).

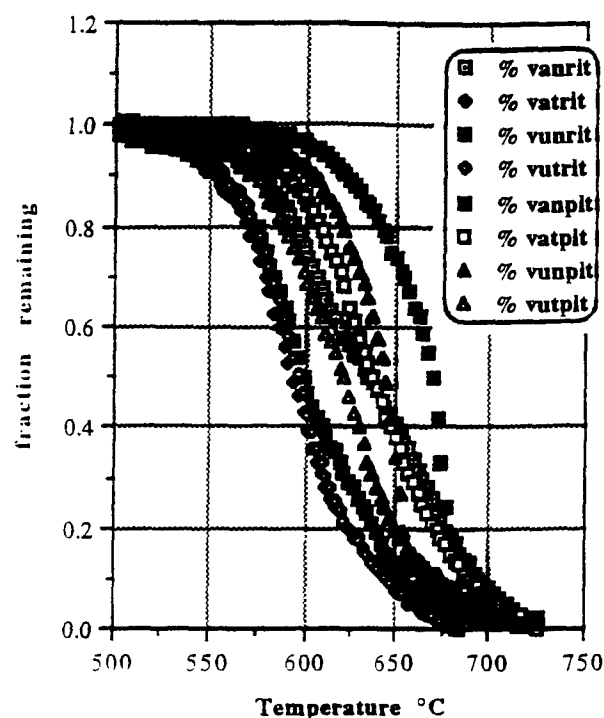


Figure 1. Burnoff of LT composites in air at a heating rate of 5 °C/min.

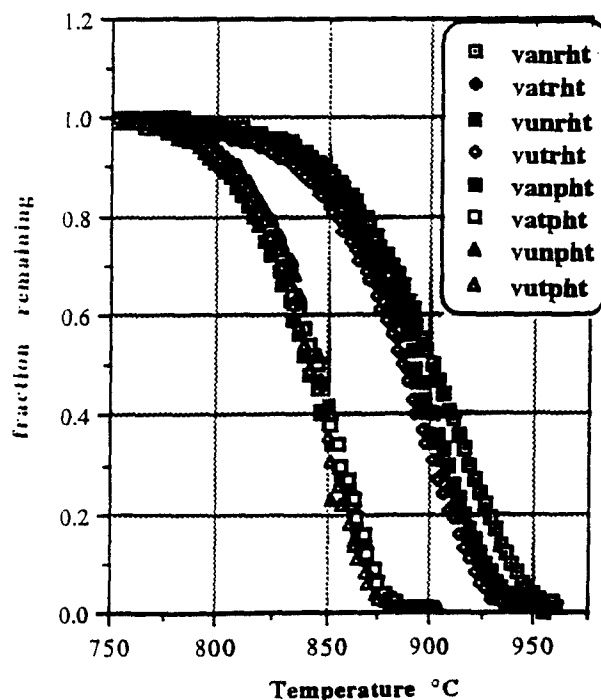


Figure 2. Burnoff of HT composites in air at a heating rate of 5 °C/min.

# CVI CARBON-CARBON COMPOSITES: FIBER-MATRIX INTERACTION EFFECTS ON OXIDATION RESISTANCE

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## INTRODUCTION

In previous studies we have examined the oxidation resistance of composites produced by chemical vapor infiltration (CVI) [1] and liquid phase impregnation (LPI) [2] of substrates of varying reactivity. One of the phenomena discovered in this effort was that upon high temperature treatment, composites produced by LPI of porous fibers were found to be more oxidation-resistant than those produced by LPI of non-porous, less reactive fibers. This effect was not observed in composites produced from CVI of similar substrates, a result that was attributed to the failure of the pyrolytic carbon to deposit in the fiber pores [3].

The present study was undertaken to see if the effect found in the LPI composites is exhibited also by CVI composites when they are produced under conditions favoring surface nucleation of pyrolytic carbon and pore filling rather than pore covering.

## EXPERIMENTAL

The substrates used in this study were two rayon-based carbon cloths (VCL and WCA, Amoco Performance Products) as received and heat treated (ht) to 2850 °C in Ar. The initial BET surface areas of the samples were less than 1 m<sup>2</sup>/g. These were activated to 40-60% burn-off in CO<sub>2</sub> in order to develop their pore structure. Propylene was used as the pyrolytic carbon matrix precursor, deposited at 750 °C at a total pressure of 10 torr for 10 hours. Matrix yields varied from ~15-30% depending upon the surface area of the substrate. After deposition, the composites were heat-treated to 2850 °C in Ar.

The pore structure of the substrates was analyzed using N<sub>2</sub> and CO<sub>2</sub> adsorption. The oxidation behavior of the composites was studied using non-isothermal thermogravimetric analysis (1 atm O<sub>2</sub>, 100 scc/min) at a heating rate of 5 °C/min.

## RESULTS AND DISCUSSION

Figure 1 summarizes the oxidation resistance of the substrates prior to CVI. Upon heat treatment the reactivity of the VCL fabric increases dramatically, while that of the WCA fabric does not change, as it had already undergone high-temperature treatment in the manufacturing process.

Upon activation, the oxidation resistance of the fabrics decreases as surface area increases. Activation of the VCL fabric to 40% burn-off increased the BET surface area to ~900 m<sup>2</sup>/g. Activation of the WCA cloth to 60% only increased the surface area to ~125 m<sup>2</sup>/g. Even less porosity was developed in the heat-treated VCL cloth, ~70 m<sup>2</sup>/g, which is reflected in its oxidation profile, as compared to the activated WCA cloth.

Figure 2 presents the oxidation profiles of the composites before heat treatment. After CVI, the oxidation resistance of the VCL-based composite increases over that of the original substrate as porosity is filled (vcl-40/10 torr vs. vcl-40% b.o.). That of the WCA-based composite increases as well (ht wca-60/10 torr vs. ht wca 60% b.o.), although it is clear from the two steps in the burn-off profile that the pyrolytic carbon matrix is more reactive than the fibers. The oxidation resistance of the heat-treated VCL/CVI composite decreased with respect to the substrate alone, indicating that the pyrolytic carbon matrix is less oxidation-resistant than the fiber. Because of the low matrix yield (~15%) it is difficult to observe any two-step behavior.

Figure 3 shows the oxidation profiles of the heat-treated composites. The oxidation resistance of all the composites increases, but the composite made from the non-heat-treated, high-surface-area VCL fabric proves to be the most oxidation resistant upon heat treatment (Figure 3a). The pyrolytic carbon matrix in the VCL-based composite is less reactive than even the WCA cloth. Once the matrix is burned away (at ~70%) the reactivity of the composite becomes lower than that of the WCA (Figure 3a).

A similar result was found in the case of LPI composites made from fibers which had not been exposed to high temperatures [3]. This was attributed to good penetration of the liquid pitch into the pores and a good coupling between the fibers and matrix. Upon heat treatment, tensile stresses at the matrix-fiber interface from matrix and fiber shrinkage and realignment [4,5] are thought to induce enhanced graphitization of the matrix and a corresponding decrease in reactivity. A low-temperature substrate such as VCL will undergo shrinkage and realignment to a higher degree than WCA or heat-treated VCL.

Although present, this synergistic effect was not found to be as pronounced for the CVI composites. This may be because the pyrolytic carbon matrix is more graphitizable than the petroleum pitch used to form the matrix in the LPI composites.

## CONCLUSIONS

As was found to be true for LPI composites, the most oxidation-resistant CVI-based composites are not necessarily made from the most oxidation resistant fibers. Optimizing the fiber porosity not only increases the matrix yield, but also may increase the oxidation resistance of the composite.

## ACKNOWLEDGMENT

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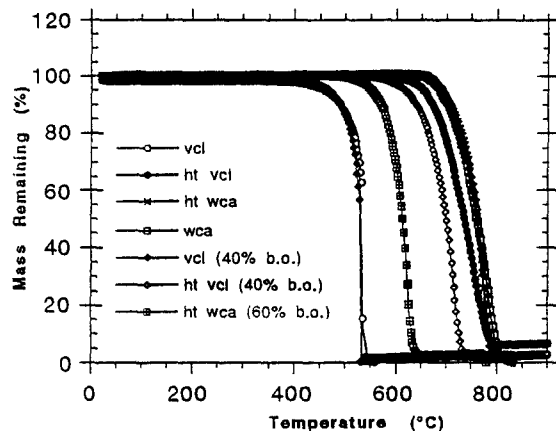


Figure 1. Oxidation profiles of different carbon cloths.

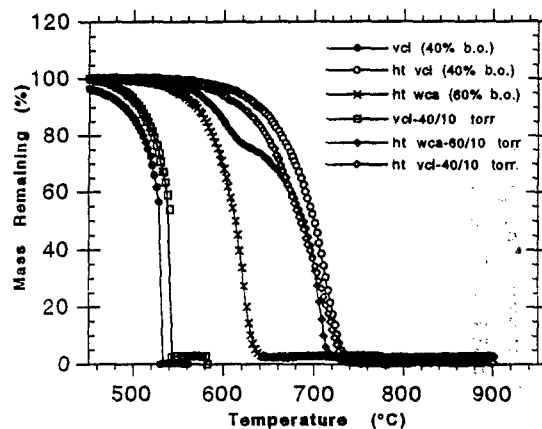


Figure 2. Oxidation profiles for low-temperature composites.

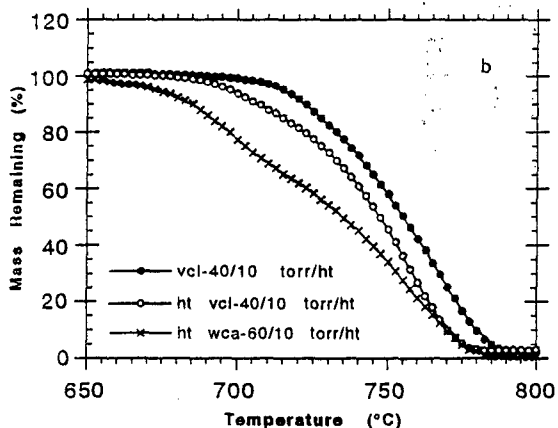
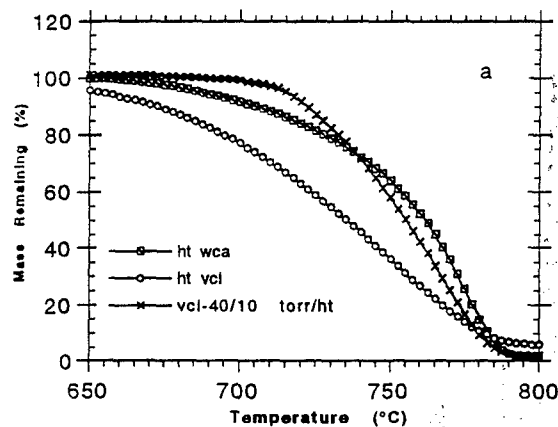


Figure 3. Oxidation profiles for high-temperature composites.